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Chemical analysis of surface and irrigation water in relation to aquatic plant management

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Chemical analysis of surface and irrigation water in relation to aquatic plant management

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SUMMARY

This publication describes water sampling techniques and analytical procedures used by the Lethbridge Research Station, Agriculture Canada, for the chemical analysis of fresh water in agriculturally associated aquatic ecosystems. Emphasis is on the nutrient parameters that influence the growth and development of nuisance aquatic vegetation. Chemical composition is also critical for the effective and environmentally safe use of herbicides in irrigation water for the management of aquatic vegetation. Recommendations are made for water sampling, sample manipulation, storage, and significance of water quality data collected as related to aquatic vegetation management.

RESUME

Cette publication décrit les techniques de prélèvement et d'analyse de l'eau en usage à la Station de recherches de Lethbridge (Agriculture Canada) pour les eaux des écosystèmes aquatiques reliés à l'agriculture. L'accent est placé sur les paramètres trophiques qui influent sur la croissance et le développement de la végétation aquatique nuisible. La composition chimique de l'eau revêt en outre une importance critique pour l'efficacité et pour l'innocuité écologique des herbicides employés pour maîtriser la végétation aquatique dans les canaux d'irrigation. L'article comporte des recommandations touchant le prélèvement des échantillons d'eau, leur manipulation et leur conservation et examine la signification des données sur la qualité de l'eau recueillies dans une optique de maîtrise de la végétation aquatique.

INTRODUCTION

If resources of land and water are to be effectively used in the provision of food, natural products, power, communications, and recreation, effort must be made to resist and, when possible, eliminate biological factors that would otherwise thwart the attainment of this goal. Awareness of this need does not excuse the clumsy and shortsighted attempts to control weeds by the indiscrete use of certain herbicides, which in the past have outraged the public. To attain successful control of aquatic weeds we must expand our knowledge of the interactions between the aquatic plant communities and their surrounding chemical and physical environments. The pattern of these interactions is extremely difficult to analyze and the various physiological, climatic, soil, and biological factors involved tend to be difficult to delineate. Environmental factors themselves interact and no single factor may be cited as the fundamental one in control of plant growth and its distribution. The general water chemistry of surface water probably determines whether a given species can grow in it. A more thorough understanding of these interactions would enable more effective use of available herbicides.

Aquatic plants require generally the same macronutrients and micronutrients that are essential for the healthy growth of terrestrial green plants. Rooted emergent aquatic plants probably obtain these nutrients from the substrate, whereas rooted submerged plants may absorb nutrients from both the substrate and the water. Free-floating species must obtain all their nutrients from the water. The nutrient ions of major metabolic significance in fresh water are those of carbonate, bicarbonate, nitrates, nitrites, total phosphorus, silica, sulfates, sulfites, chlorides, potassium, sodium, calcium, and magnesium. Trace ions essential to the growth of aquatic plants but required only in extremely small quantities include those of iron, copper, boron, molybdenum, cobalt, manganese, zinc, and iodine. Logically, the first step toward an understanding of the interactions involved in the control of aquatic plant growth must be the rapid and precise analysis of surface and irrigation waters to determine the concentration of the nutrients listed above. This manual has been prepared as a guide to the gathering of this information. The methods represent the best known procedures with respect to accuracy, speed, ease of manipulation, and cost of equipment necessary for analysis.

The following references are suggested as sources of general chemical anaysis procedures and references on aquatic plant taxonomy, physiology, and biochemistry:-

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Ward, G. M. and F. B. Johnston. 1962. Chemical methods of plant analysis. Queen's Printer, Ottawa.

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SAMPLING TECHNIQUE AND SAMPLE PREPARATION

Samples are collected and stored for short periods of time in polyethylene bottles of 500-mL or 1-liter size. This has proved to be the most satisfactory method as the bottles are easy to transport, light in weight, and convenient to handle. Samples that are not analyzed immediately are frozen solid at a temperature not exceeding -20°C. Unless they are overfilled, the polyethylene bottles will not break when the samples freeze. For studies on the stratification of lakes and rivers, a 1-liter Van Dorn sampler is used. By immersing a mercury thermometer in the sampler as soon as it reaches the surface, the in situ temperature of the sample can be estimated within one or two degrees. Alternatively, since both plexiglass and PVC are fairly poor conductors of heat, a thermometer mounted in the sampler will provide an equally close estimate of the temperature of the sample. Samples should be recovered and temperatures read without undue delay.

Samples received at the laboratory for analysis within a few hours of collecting are not treated with preservatives. If the analysis cannot be started within 12 hours of collecting, sulfuric acid or formaldehyde is added to prevent the growth of organisms that might cause alteration of the sample.

The collecting bottles should be thoroughly cleaned with dichromate cleaning solution. They should be rinsed thoroughly first with tap water and then with three changes of distilled water. If a good detergent is used for cleaning, the bottles should be washed with 2 N hydrochloric acid, then rinsed thoroughly with tap water and three changes of distilled water. Prior to filling, the sample bottle should be rinsed out two or three times with the water to be collected. Generally, representative samples are obtained by combining samples collected at a number of different sampling points. It is impossible to give instructions covering all conditions that may be encountered. Since biweekly samples should be analyzed to provide a working knowledge of the body of water under study, some form of data reporting is necessary. We have found the following method convenient. At the time of sample collecting, temperature, dissolved oxygen, pH, carbonate content, and light transmission measurements are recorded. The plant communities as they appear are recorded at the time of each collection although the total pattern may not become evident until the end of the season. The following outline lists the information one can obtain from a single lake sampling along with the equipment used.

Ion concentrations are recorded in parts per million (ppm), which is the equivalent of milligrams per liter. While ppm is the most satisfactory unit for our work, water standards are often reported as milliequivalents per million (meqpm). The conversion of ppm to meqpm is given in the calculations section for each element.

EQUIPMENT AND CHEMICALS

The usual standard laboratory glassware and apparatus are used for the analyses reported here. A centrifuge capable of handling both 15-mL and 50-mL centrifuge tubes is useful. A sensitive analytical balance is necessary as well as a number of hot plates with variable temperature control. Some of the procedures outlined here are colorimetric; therefore, a good spectrophotometer is necessary. We use a Bausch and Lomb Spectronic 2000. A spectrophotometer equipped with a printer and autosampler speeds up the collection of analytical data when many samples are being processed. For rapid determination of certain ions and radicals, a specific ion meter is most useful. For this purpose, we use a model 404 Orion Ionanalyzer that is equipped to record pH, absolute potential in millivolts, and monovalent and divalent anions and cations. The advantages of this instrument are that it has solid state circuitry, readings are made directly, it is portable and the readings are reproducible. Other pieces of equipment that may be useful are a conductivity bridge, atomic absorption spectrophotometer, and light recording meter.

All the reagents named on the following pages are of Reagent grade or better quality. For very sensitive procedures, it is sometimes necessary to redistill the solvents in an all-glass distillation apparatus. Distilled water is used exclusively. A supply of redistilled water is also kept on hand. Concentrations of reagent solutions expressed as percentage values are made by dissolving the solid reagent in water diluted to a particular concentration with the designation w/v.

The largest single investment is the chemicals for analytical use. But once these are purchased, they will not, in most cases, need to be reordered for a number of years.

ATOMIC ABSORPTION SPECTROPHOTOMETRY

Description

A rapid, very sensitive alternative method for the quantitative determination of trace elements and major cations in a solution form.

Principle

Atomic absorption spectroscopy is the measurement of the amount of radiant energy absorbed by unexcited (ground state) atoms of that element at a reasonance wavelength of that particular element. Since approximately 99% of the atoms are in an unexcited state when aspirated into the flame, they readily absorb light, rather than emit it. Therefore, the absorption of light due to a transition from the ground state to a higher energy level by the electrons of the element being determined; it is almost an absolute measurement of the number of atoms contained within a given sample.

Equipment

All atomic absorption spectrophotometers contain the same basic components.

1) Radiant energy source
   Usually a hollow cathode lamp which may be single or multi in element(s). The lamps are connected to a power supply unit to stabilize the lamp current.

2) Atomizer and burner
   A chamber where the sample (solution) is taken up to form an aerosol before burning takes place in the flame. Gases are fed to the burner by a controlled unit so that variable ratios of fuels can be achieved.

3) Monochromator
   Consists either of a prism or grating. The latter being preferred for the separation of reasonance line(s) of an element.

4) Detector
   Usually in the form of a photomultiplier that covers the ultraviolet and visible light wavelength ranges.

5) Amplifiers and readout units
   Either a log (absorbance) or % transmittance scale. Additional equipment can be added so that readouts are in a digital form with computerized linkages.

Analytical Parameters

To determine the maximum absorption of an element, the following constituents are very important. Manufacturers of instruments usually supply values for optimum operating conditions of their instrument. Parameters to consider are:

1) Lamp current
2) Fuel ratios
3) Height of plane at the flame
4) Width of the flame
5) Slit width
6) Wavelength

SPECIFIC ION ACTIVITY METER AND ELECTRODES

Specific ion electrodes measure the single ion activity of an ion in solution rather than the concentration of the ion. The activity of an ion in solution is the measure of the reactivity of the ion (the extent and rate to which the ion takes part in the chemical reaction). In dilute solutions, the activity of an ion approaches the concentration. Therefore, in many cases, the activity is proportional to the concentration, allowing the electrode to be calibrated in terms of concentration.

All specific ion electrodes are subject to interferences from other ions. Cation electrodes are usually subject to interferences from other cations and anion electrodes to interferences from other anions. Many interferences can be removed by adjusting the sample pH or by precipitating or complexing the interfering ion.

The lower limit of detection is usually determined by the solubility of the sensing element or the liquid ion exchanger in the electrode. The pH of the solution sometimes determines the lower limit of detection.

The upper limit of detection for solid state electrodes is the saturated solution. However, due to the problems of taking measurements without large reference electrode erros (junction potentials), the electrode is specified as having an upper limit of 1 molar.

The upper limit of detection for liquid membrane electrodes is determined by the level at which there is an appreciable solubility of the ions from the sample into the ion exchange phase of the electrode.

ANALYSIS OF NUTRIENT ELEMENTS

1. NITRATES (NO_3) BY SPECTROPHOTOMETRY

Nitrate is the most common form of nitrogen found in lakes from the surface to the lake bottom. Ammonia can occur from the decomposition of plant and animal protein but in the presence of oxygen, is rapidly transformed by nitrifying bacteria into nitrate. During the winter when the oxygen levels fall rapidly the nitrite concentration increases but once the ice breaks-up in the spring the action is reversed. In highly eutrophic lakes there can be an decrease in nitrate and an increase in nitrite as a result of the lower oxygen levels and the action of denitrifying bacteria.

Reagents

1) Standard silver sulfate solution
   Dissolve 4.4 g Ag_2SO_4 in distilled water and dilute to 1.0 liter; 1.0 mL = 1.0 mg Cl.

2) Phenoldisulfonic acid reagent
   Dissolve 25 g pure white phenol in 150 mL concentrated H_2SO_4 (sp gr 1.84). Add 75 mL fuming H_2SO_4 (15% free SO_3), stir well, and heat for 2 hours on a hot water bath.

3) Ammonium hydroxide concentrate

4) 12N KOH
   Dissolve 673 g KOH in distilled water and dilute to 1.0 liter.

5) EDTA reagent
   Rub 50 g disodium ethylenediamine tetraacetate dihydrate, also called ethylenedintrilo tetraacetic acid sodium salt, with 20 mL distilled water to form a thoroughly uniform paste. Add 60 mL concentrated NH_4OH and mix well to dissolve the paste.

6) Stock nitrate solution
   Dissolve 0.7218 g anhydrous potassium nitrate, KNO_3, and dilute to 1.0 liter with distilled water. Solution = 100 mg/L N.

7) Standard nitrate solution
   Evaporate 50 mL stock nitrate solution to dryness on a steam or hot water bath. Dissolve the residue formed by rubbing it with 2 mL phenoldisulfonic acid reagent, and dilute to 500 mL with distilled water. 1.0 mL = 10 µg N = 44.3 µg NO_3.

8) Aluminum hydroxide suspension
   Dissolve 125 g potassium or ammonium alum, $K_2Al_2(SO_4)_4 \cdot 24H_2O$ or $(NH_4)_2Al_2(SO_4) \cdot 24H_2O$ in 1.0 liter of distilled water. Warm to 60°C and add 55 mL concentrated NH_4OH slowly, with stirring. After

permitting the mixture to stand about 1 hour, transfer it to a large bottle and wash the precipitate by successive additions (with thorough mixing) and decantations of distilled water until free from ammonia, chloride, nitrite, and nitrate.

9) Sulfuric acid (1N)
Add 28 mL concentrated H_2SO_4 to distilled water and dilute to 1.0 liter.

10) Potassium permanganate (0.1N)
Dissolve 0.316 g $KMnO_4$ in distilled water and dilute to 100 mL.

11) Dilute hydrogen peroxide solution
Dilute 10 mL 30% H_2O_2 (low in nitrate) to 100 mL with distilled water.

12) Sodium hydroxide (1N)
Dissolve 40 g NaOH and dilute to 1.0 liter with distilled water.

Calibration Curve

1) Add 0.0, 5, 15, 25, 35, 50, 75, 100 mL of standard nitrate solution to 100 mL volumetrics and dilute to the mark with distilled water.

2) Follow steps 1 to 10 of the procedure for nitrate samples.

3) Draw a calibration curve of absorbance vs nitrate concentration (µg/mL).

4) To convert nitrate concentrations from parts per million to milli-equivalents per million multiply ppm by 0.016.

Sample Procedure

1) Color removal
If the sample has a color of more than 10, decolorize it by adding 3 mL $Al(OH)_3$ suspension to 150-mL sample. Stir the sample thoroughly, allow to stand for a few minutes, then filter, discarding the first portion of the filtrate.

2) Nitrite conversion
To 100-mL sample add 1.0 mL H_2SO_4 and stir. Add dropwise either $KMnO_4$ or H_2O_2 solution, stirring the solution constantly. Let the treated sample stand for 15 min to complete the conversion of nitrite to nitrate (a faint pink color persists for at least 15 min when sufficient $KMnO_4$ is used).

3) Chloride removal
   Determine the chloride content of the water (refer to method for chlorides) and treat 100-mL sample with an equivalent amount of standard Ag_2SO_4 solution. Remove the precipitated Cl^- by filtration. (Coagulation of the AgCl will occur by heat or by leaving it overnight at 25°C in the dark.

4) Neutralize the clarified sample to pH 7, transfer to a casserole and evaporate to dryness over a hot water bath.

5) Using a glass stirring rod, rub the residue thoroughly with 2 mL phenoldisulfonic acid reagent to dissolve all solids.

6) If required, heat mildly on a hot water bath a short time to dissolve the entire residue.

7) Dilute the sample with 20 mL distilled water and add, with continuous stirring, 6 to 7 mL NH_4OH or 5 to 6 mL KOH (12N) until maximum color is developed.

8) Remove any resulting flocculent hydroxides by passing through a filter paper or add EDTA reagent with stirring until the turbidity redissolves.

9) Transfer the filtrate or clear solution to a 50-mL volumetric flask and dilute to the mark and mix.

10) Take the % transmittance of the solution at 460 mμ against a blank of phenoldisulfonic acid reagent and NH_4OH or KOH as used for samples (sample volumes).

11) Read the unknown values from the calibration curve.

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Standard methods for the examination of water and sewage. 1949. Ninth edition. American Public Health Association, Inc., New York.

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Welcher, F. J. 1966. Standard methods of chemical analysis. Vol. IIIB. D. Van Nostrand Co., Inc., Princeton, New Jersey.

2. NITRATES (NO_3) BY SPECIFIC ION ELECTRODES

Reagents

1) Ammonium sulfate ionic strength adjustor (ISA)
   Dissolve 26.4 g $(NH_4)_2 SO_4$ in distilled water and dilute to 100 mL with distilled water.

2) Reference electrode (outer chamber) filling solution
   Dilute 2 mL of ISA to 100 mL with distilled water.

Solutions

1) Sodium nitrate 1000 ppm NO_3
   Dissolve 1.3708 g of $NaNO_3$ and dilute to 1.0 liter with distilled water.

2) Make a series of of standard solutions by diluting 1000 ppm NO_3 to obtain concentrations at 0.1, 1.0, 10, and 100 ppm NO_3.

Procedure

1) Pipette 20 mL of standard solution into a 50-mL beaker.

2) Add 0.4 mL of ISA solution to each standard.

3) Stir the sample and take an electrode reading from the specific ion meter, which has been set up to the manufacturers instructions, on the millivolt scale (mv).

4) Plot the readings obtained for each standard on semilog graph paper to obtain a standard curve (conc. NO_3 ppm vs. mv).

5) For each sample, do steps 1 to 3, then determine the concentration of NO_3 from the standard curve.

References

Durst, Richard A. (editor). 1969. Ion-selective electrodes. National Bureau of Standards, Special Publication 314.

Milham, P. J., A. S. Awad, R. E. Paull and J. E. Bull. 1970. Analysis of plants, soils, and waters for nitrate by using an ion-selective electrode. Analyst 95: 751-757.

Shaw, E. C. and P. Wiley. 1969. Nitrate ion concentration in well water. California Agriculture. May 1969.

3. NITRITES (NO_2) BY SPECTROPHOTOMETRY

Reagents

1) Sulfanilamide
   Dissolve 5 g sulfanilamide compound $NH_2SO_2C_6H_4NH_2$, in 500 mL 1.2N HCl and store in an amber bottle.

2) Coupling reagent: N-(1-naphthyl) etyhlenediamine dihydrochloride, 0.1% solution
   Dissolve 0.50 g $C_{10}H_7NHCH_2CH_2NH_2 \cdot 2HCl$ in distilled water and dilute to 500 mL. Store in an amber glass bottle.

3) Standard nitrite solutions

   Solutions:

   a) Dry pure sodium nitrite at 110°C for 2 hours and cool in a desiccator. Dissolve 0.3450-g dried compound in distilled water and dilute to 1.0 liter. Add a few drops chloroform to prevent bacterial growth. 1.0 mL = 5 µg at NO_2-N.

   b) Dilute 5 mL solution A to 500 mL with distilled water. Each mL = 0.05 µg at NO_2-N.

   c) Prepare standard solutions of 0.05 - 1.0 µg at NO_2-N/L as needed by diluting 1-10 mL of solution B to 1.0 liter.

Calibration Curve

1) Prepare standards by pipetting 1-10 mL solution B and diluting each to 1.0 liter with distilled water.

2) Pipette 50 mL each solution into beakers and add 1.0 mL sulfanilamide solution and mix thoroughly.

3) After 5 minutes, add 1.0 mL coupling reagent solution. A maximum color development will occur after about 10 minutes.

4) Measure the % transmittance at 540.3 mµ using distilled water as a blank.

5) Draw a calibration curve of absorbance vs nitrite concentration (µg/l).

6) To convert nitrite concentrations from parts per million to milli-equivalents per million, multiply ppm by 0.0217.

Sample Procedure

1) Pipette 50 mL of sample into a 100-mL beaker.

2) Heat the sample to approximately 50°C.

3) Add 1.0 mL sulfanilamide solution and mix thoroughly.

4) Follow steps 3 and 4 of the procedure for the calibration curve.

5) From the calibration curve, determine the concentration of the unknown nitrite concentration of the sample.

References

Martin, D. F. 1968. Marine chemistry. Vol. I. Analytical methods. Marcel Dekker, Inc., New York.

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4. AMMONIA (NH_3) BY SPECIFIC ION ELECTRODES

Reagents

1) Ammonium chloride 100 ppm NH_3
   Dissolve 0.0198 g of NH_4Cl and dilute to 1.0 liter with distilled water.

2) 10M Sodium hydroxide
   Add distilled water to 100 g of NaOH pellets. Cool and dilute the solution to 250 mL with distilled water.

Standards

1) Make a series of dilutions to obtain solutions at 0.1, 0.5, 1.0, 5, and 10 ppm NH_3 from the 100 ppm NH_3.

Procedure

1) Pipette 25.0 mL of solution into a 50 mL beaker.

2) Add 0.25 mL of 10M NaOH to the solution immediately before reading the sample.

3) Stir the sample for approximately one minute, then take an electrode reading, which has been set up to the manufacturer's instructions, on the millivolt scale (mv).

4) Plot the readings obtained for the standards on semilog graph paper to obtain a standard curve concentration NH_3 (ppm) vs mv.

5) For samples, do steps 1 to 3, then determine the concentration at NH_3 from the standard curve.

References

Glasstone, S. 1946. Textbook of Physical Chemistry, Van Nostrand, N.Y.

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Ringbom, A. 1963. Complexation in analytical chemistry. Interscience, New York.

5. TOTAL PHOSPHATES (PO_4) BY SPECTROPHOTOMETRY

During the past two decades, a great deal of attention has been given to the phosphorus content of lakes and streams, both before and after pollution. The soluble phosphorus content in natural, unmodified waters is small and since phytoplankton requires an adequate supply of phosphorus, it is generally regarded as a limiting factor. Phosphorus is essential in the metabolism of phospholipids, sugar phosphate, coenzymes, nucleic acids, nucleotides, and proteins. Phosphates play a key role in plant energy transfers. Extensive studies based upon measurements in natural waters and the addition of small amounts of phosphorus fertilizers should supply vital data on the importance of phosphorus. Large quantities of phosphorus are excreted from beef cattle during feedlot operations. The annual excretion of phosphorus from 100 cows with an average weight of 450 kg is approximately 900 kg of phosphorus. The use of polyphosphates in detergents is another source of contamination.

Very recent research has drawn attention to the possibility of the importance of the ratio of nitrogen to phosphorus. This is one of the important interactions that need further study in inland waters. Once this reaction has been investigated, it may prove useful to investigate other and more complicated ratios, such as carbon-nitrogen-phosphorus and oxygen-carbon-nitrogen-phosphorus.

Reagents

1) Phenolphthalein indicator
   Dissolve 5 g phenolphthalein in 500 mL 95% ethanol. Add approximately 490 mL distilled water. Add 0.02N NaOH dropwise until a faint pink color appears. Dilute to 1.0 liter.

2) Strong-acid solution
   Cautiously add 300 mL concentrated H_2SO_4 to about 600 mL distilled water. When the solution is cool, add 4 mL concentrated nitric acid and dilute to 1.0 liter.

3) a) Sodium hydroxide (1N)
      Dissolve 40 g NaOH in a small quantity of distilled water. Cool and dilute to 1.0 liter.

   b) Sodium hydroxide (10N)
      Dissolve 400 g NaOH in distilled water. Cool, dilute to 1.0 liter with distilled water.

4) Ammonium molybdate reagent
   Dissolve 25 g $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ in 175 mL distilled water. Cautiously add 280 mL concentrated H_2SO_4 to 400 mL of distilled water. Cool, add the molybdate solution, and dilute to 1.0 liter.

5) Stannous chloride reagent
Dissolve 2.5 g $SnCl_2 \cdot 2H_2O$ in 100 mL glycerin. Heat the solution in a water bath to aid dissolution.

6) Stock phosphate solution
Dissolve 0.7165 g anhydrous potassium dihydrogen phosphate, KH_2PO_4, in distilled water and dilute to 1.0 liter. 1.0 mL = 0.5 mg PO_4.

7) Standard phosphate solution
Dilute 100 mL stock phosphate solution to 1.0 liter with distilled water. 100 mL = 50 µg PO_4.

Calibration Curve

1) Pipette 0, 0.1, 0.3, 0.5, 0.7, 1.0, and 1.5 mL of standard phosphate solution into 100-mL volumetric flasks and dilute to the mark.

2) Pour the solutions into 250-mL beakers.

3) Add 1 drop phenolphthalein. If a red color appears, add strong-acid solution until the solution becomes colorless. Then add 1.0 mL of excess of the strong-acid solution.

4) Boil the solution gently for 2 hours retaining a volume of 25-50 mL.

5) Cool the solution, then neutralize it with NaOH until a faint pink color persists.

6) Make the solution up to its original volume of 100 mL.

7) Add 1 drop strong-acid solution or up to 5 drops. If more than 5 drops are required, take an aliquot and dilute it to 100 mL.

8) Add 4 mL molybdate reagent and 10 drops stannous chloride reagent and mix thoroughly.

9) After 10 minutes, but before 12 minutes, measure the % transmittance of each solution at 690 mµ.

10) Plot a graph of absorbance vs concentration of phosphate (ppm).

11) To convert phosphate concentrations from parts per million to milli-equivalents per million, multiply ppm by 0.0316.

Sample Procedure

1) If the sample is turbid, two (2) 100-mL samples must be taken.

2) Filter one (1) 100-mL sample.

3) Follow steps 3 to 9 inclusive of the procedure for the calibration curve.

4) Read the sample concentration off the graph.

Reference

Standard methods for the examination of water and waste water including bottom sediments and sludges. 1976. Fourteenth edition. American Public Health Association, Inc., New York.

6. TOTAL PHOSPHATES (P - PO_4) BY PERCHLORIC ACID DIGESTION AND SPECTROPHOTOMETRY

Reagents

1) Sulfuric acid (9N)
   Carefully pour 250 mL concentrated H_2SO_4 (sp gr 1.84) into 250 mL of distilled water and allow the solution to cool to room temperature. Readjust the volume after cooling to make a 9N solution.

2) Ammonium molybdate-sulfuric acid solution
   Dissolve 15 g ammonium molybdate $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ in 150 mL distilled water. (If the solution is not clear, filter the solution until a clear filtrate is obtained.) Pour the molybdate solution into 450 mL 9N H_2SO_4. Store in an amber bottle or in the dark.

3) Cold boiled-out distilled water
   Boil distilled water for 10 minutes, cool, cover with a watch glass, and store in a tightly closed container.

4) 5% HCl
   Add 50 mL concentrated HCl to cold boiled-out distilled water and dilute to 1.0 liter.

5) Stannous chloride stock solution
   Dissolve 4.3 g $SnCL_2\cdot 2H_2O$ in 10 mL concentrated HCl (sp gr 1.19) and dilute to 100 mL with cold boiled-out distilled water. Then place 10 mL petroleum ether on top of the solution.

   Dilute solution
   Dilute 5 mL stock stannous chloride solution to 25 mL with 5% HCl (v/v). Prepare this solution freshly each day.

6) Standard phosphate solution
   Dissolve 0.34 g KH_2PO_4 in distilled water and dilute to 1.0 liter. This solution contains 2.5 µg PO_4-P/mL. This solution should be stable for 1 month. Add 1.0 mL CCl_4 to inhibit the growth of molds or bacteria.

   Dilute solution of phosphate
   Dilute 10 mL standard phosphate stock solution to 1.0 liter with distilled water. This solution contains 0.0025 µg of PO_4-P.

7) Perchloric acid
   Reagent grade 60% acid.

8) Sodium hydroxide (10N)
Dissolve 80 g reagent grade NaOH in distilled water, cool, and dilute to 200 mL.

9) HCl (12N)
Concentrated acid (sp gr 1.19)

Calibration Curve

1) Dilute 0.0, 0.2, 0.5, 0.7, 1.0, 1.5, 2, 3, 4, 5, 7, and 10 mL dilute solution of phosphate to 100 mL with distilled water.

2) Filter the solutions and take a 50-mL aliquot and place it in a 125-mL Erlenmeyer flask.

3) Add 3 mL 60% perchloric acid to the sample.

(WARNING! Perchloric acid can be explosive. Care must be exercised at all times. Fume hoods should be designed to permit routine cleaning.)

4) Evaporate the sample on a hot plate until the fuming temperature of perchloric acid is reached and white fumes are noted.

5) Place a watch glass on the flask and heat the contents of the flask for 5 minutes below the fuming temperature.

6) Remove the flask from the hot plate and cautiously add 3 mL HCl (12N) to the contents of the flask.

7) Replace the flask on the hot plate and fume off rapidly. This should remove any interfacing arsenic present.

8) Allow the flask to cool. Add 30 mL distilled water to dissolve any salts formed.

9) Neutralize the excess acid present by adding 10N sodium hydroxide until the solution is neutral to wide range pH paper (1-14).

10) Slightly acidify the solution with dilute HCl.

11) Dilute the solution to 50 mL in a volumetric and mix thoroughly.

12) Add 1.0 mL ammonium-molybdate-sulfuric acid solution and after 3 minutes, add 4 drops dilute stannous solution and mix thoroughly.

13) Five (5) minutes after the addition of stannous chloride, read the % transmittance at 705 mμ using a solution containing 0.01 mL phosphate solution as a blank.

14) Draw a calibration curve of absorbance vs phosphate concentration ($\mu g/mL$ = ppm = mg/L).

15) To convert phosphate concentration from parts per million to milli-equivalents per million, multiply ppm by 0.0316.

Sample Procedure

1) Follow steps 2 to 13 inclusive of the procedure for the calibration curve.

2) From the absorbance, determine the unknown concentration of the sample off the calibration curve.

Reference

Martin, D. F. 1968. Marine chemistry. Vol. 1. Analytical methods. Marcel Dekker, Inc., New York.

7. SILICATES (SiO_2) BY SPECTROPHOTOMETRY

Diatoms require silicon for the construction of their hard shells and since they constitute a very prominent and strategic group in the phytoplankton in nature, an available supply of silicon in the water is regarded as a matter of real importance. Fresh-water sponges also depend upon an adequate supply of silicon for the manufacture of spicules. Higher plants seem to profit by the presence of silicon and may also act as consumers. The interaction with iron, copper, manganese, and phosphate requires a good deal more research. It appears that the silicon cycle in natural waters is still a partial mystery.

A) SILICA I (at 410 m)

Reagents

1) Ammonium molybdate solution
   Dissolve 10 g of $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ per 100 mL of distilled water.

2) HCl
   Dilute 1:1 with distilled water.

3) Oxalic acid solution
   Dissolve 10 g $C_2H_2O_4\cdot 2H_2O$ per 100 mL of distilled water.

4) Sodium silicate standard solution
   Fuse 3 g sodium carbonate, Na_2CO_3, with 0.20 g pure dry silica in a platinum crucible. Dissolve in 200 mL of distilled water and dilute to 1.0 liter with distilled water.

5) Alternate standards using potassium chromate
   Dissolve 0.63 g K_2CrO_4 in 1.0 liter of distilled water.

6) Sodium tetraborate 1%
   Dissolve 10.0 g in 1.0 liter distilled water.

Calibration Curve I(a)

1) Pipette 1.0, 2, 3, 4, 5, 7, 10, 15, and 20 mL of standard silica into 100-mL volumetrics and dilute with distilled water.

2) Pipette 50 mL of each solution into 100-mL beakers.

3) Quickly add in succession 2 mL of $(NH_4)_6Mo_7O_{24}$ solution and 1.0 mL dilute HCl.

4) After 5 min add 2 mL $C_2H_2O_4$ solution.

5) Read the % transmittance at 410 mμ of each solution against a reagent blank.

6) Prepare a calibration curve from the resultant values and plot absorbance vs silica concentration (ppm).

7) To convert silica concentrations from parts per million to milli-equivalents per million, multiply ppm by 0.0263.

Calibration Curve I(b)

1) Pipette 1.0, 2, 3, 4, 5, 7.5, and 10 mL of the K_2CrO_4 solution into 25-mL volumetrics and dilute the solutions with 1% sodium tetraborate solution.

2) Pour the solutions into 100-mL beakers and dilute each solution to a total volume of 55 mL with distilled water.

3) Read the % transmittance of the solutions at 410 mμ with a blank of distilled water.

Permanent Color Standards

Potassium chromate (in 55 mL)	Equivalent ppm silica
1.0	2
2.0	4
3.0	6
4.0	8
5.0	10
7.5	15
10.0	20

4) Draw a calibration curve of absorbance vs silica concentration (ppm).

Sample Procedure

1) Pipette a 50-mL sample into a 100-mL beaker.

2) Follow steps 3 to 5 inclusive of the procedure for the calibration curve.

3) Read the sample value off the calibration curve.

B) SILICA II (AT 620 mμ) FOR TANNINS INTERFERENCE

Reagents

1) HCl 0.248N
   Add 20.5 mL concentrated HCl to distilled water and dilute to 1.0 liter.

2) Ammonium molybdate solution
   Dissolve 102 g $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ in 1.0 liter of distilled water.

3) Sodium sulfite solution
   Dissolve 170 g Na_2SO_3 in 1.0 liter of distilled water.

Calibration Curve II

1) Pipette 1.0, 2, 3, 4, 5, 7, 10, 15, and 20 mL of silica stock solution from the procedure in Silica I and dilute to 100 mL.

2) Pipette 10-mL solution into 50-mL beakers.

3) Add 5 mL 0.248N HCL and mix thoroughly.

4) Add 5 mL $(NH_4)_6Mo_7O_{24}$ solution.

5) After 1 min, add 10 mL Na_2SO_3 solution and mix.

6) Read the % transmittance at 620 mμ of the solutions against a reagent blank.

7) Prepare a calibration curve of absorbance vs silica concentration (ppm).

Sample Procedure

1) Pipette a 10-mL sample into a 50-mL beaker.

2) Follow steps 3 to 6 of the procedure for the calibration curve.

3) Read the concentration of the sample off the graph.

Reference

Standard methods for the examination of water and waste water including bottom sediments and sludges. 1976. Fourteenth edition. American Public Health Association, Inc., New York.

ANALYSIS OF MAJOR CATIONS

1. POTASSIUM (K) AND SODIUM (Na) BY ATOMIC ABSORPTION

Reagents

1) Potassium 1000 ppm
   Dissolve 1.907 g of previously dried potassium chloride in distilled water and dilute to 1.0 liter with distilled water.

2) Sodium 1000 ppm
   Dissolve 2.542 g of previously dried sodium chloride in distilled water and dilute to 1.0 liter with distilled water.

Standards

1) Prepare a set of standard solutions containing 0.5, 1.0, 2, 4, and 6 ppm K and Na.

Samples

1) Most samples require no dilution for this analysis.

Parameters

1) Potassium
   Wavelength nm 766.5
   Lamp current mA 7
   Bandpass nm 1.0
   Flame description - air-acetylene
   - oxidizing, fuel lean, blue

2) Sodium
   Wavelength nm 589.0
   Lamp current mA 8
   Bandpass nm 0.50
   Flame description - air-acetylene
   - oxidizing, fuel lean, blue

References

Butler, L. R. P. and D. Brink. 1963. The determination of magnesium, calcium, potassium, sodium, copper, and iron in water samples by atomic absorption spectroscopy. South African Industrial Chemist 17: 153.

Robinson, J. W. 1966. Atomic absorption spectroscopy. Marcel Dekker, Inc., New York.

2. CALCIUM (Ca) AND MAGNESIUM (Mg) BY TITRATION

Calcium is required by all green plants except some of the lower algae. Fungi do not require it. Calcium appears in a higher concentration in flowering plants that bear chlorophyll than in those that do not. Calcium and magnesium are intimately involved with carbonates in the production of marl or lime accumulation precipitated by plants. The productivity of the lake appears to be closely tied to the calcium and magnesium levels. It would appear that calcium performs at least five physiological functions: 1) the translocation of carbohydrates; 2) the structural incorporation in plant tissue; 3) making physiologically available other indispensable nutrient ions; 4) acting as a cofactor of enzymes involved in ATP and phospholipid metabolism; and 5) as the antidoting agent reducing the toxic effects of single salt solutions of sodium, potassium, and magnesium.

Magnesium is a component of chlorophyll and must be present for the proper development of green plants. This function alone makes the ion indispensable. In some instances, the magnesium may also act as a carrier of phosphorus and is a component of a number of enzymes involved in phosphate transfer in the cell.

Reagents

1) EDTA
   Dry the purified dihydrate ($Na_2H_2Y \cdot 2H_2O$, F.W. = 372.3) at 80°C for 2 hours to remove excess moisture. Cool. Weigh 2 g, dissolve in distilled water, and dilute to 1.0 liter.

2) Buffer pH 10
   Dilute 570 mL aqeous ammonia (sp gr 0.90) and 70 g ammonium chloride, NH_4Cl, to 1.0 liter with distilled water.

3) 1N NaOH
   Dissolve 40 g NaOH in 1.0 liter of distilled water.

4) Eriochrome black T indicator solution
   Mix 0.5 g of indicator with 4.5 g hydroxylamine hydrochloride. Dissolve this mixture in 100 mL 95% ethanol.

5) Eriochrome blue-black R
   Grind 0.2 g indicator with 100 g NaCl to 40-50 mesh.

6) Hydroxylamine hydrochloride.

Sample Procedure

1) Pipette two (2) suitable size aliquots of sample into two separate Erlenmeyer flasks.

2) Add 2 mL pH 10 buffer and 3 drops Eriochrome black T indicator solution to one of the flasks.

3) Titrate with standard EDTA solution. A color change from red to blue will occur.

4) This titration gives both Mg and Ca. Record volume as V_1.

5) To the second aliquot, add 2 mL 1N NaOH and 0.1 to 0.2 g Eriochrome blue-black R.

6) Titrate the sample to a blue end point.

7) This titration gives Ca present. Record volume as V_2.

Calculations

1) Subtract V_2 from V_1. The resultant volume (V_3) is due to the presence of Mg in the sample.

2) 1 formula wt EDTA reacts with 1 formula wt Ca or Mg.

V_2 = Ca in sample

$$\text{ppm Ca} = \frac{V \times N \times \text{eq wt} \times 1000}{\text{sample volume}}$$

$$= \frac{V \times N \times 20.40 \times 1000}{\text{sample volume}}$$

$$\text{eq wt Ca} = \frac{40.08}{2} = 20.04$$

3) $$\text{ppm Mg} = \frac{V \times N \times \text{eq wt} \times 1000}{\text{sample volume}}$$

$$= \frac{V \times N \times 27.47 \times 1000}{\text{sample volume}}$$

$$\text{eq wt Mg} = \frac{54.94}{2} = 27.47$$

4) $$\text{N EDTA} = \frac{(\text{mg EDTA} \times \text{purity factor})/\text{eq wt}}{1000 \text{ mL}}$$

$$\text{eq wt EDTA} = \frac{372.24}{2} = 186.12$$

5) To convert calcium concentrations from parts per million to milli-equivalents per million, multiply ppm by 0.0499.

To convert magnesium concentrations from parts per million to milli-equivalents per million, multiply by 0.0822.

References

Skoog, D. A. and D. M. West. 1966. Fundamentals of analytical chemistry. Holt, Rinehart, and Winston, New York.

Standard methods for the examination of water and waste water including bottom sediments and sludges. 1976. Fourteenth edition. American Public Health Association, Inc., New York.

3. CALCIUM (Ca) AND MAGNESIUM (Mg) BY ATOMIC ABSORPTION

Reagents

1) Calcium 1000 ppm
   Disperse 2.497 g of previously dried calcium carbonate in 50 mL of distilled water. Add drop by drop a minimum volume of concentrated hydrochloric acid until complete dissolution of the $CaCO_3$. Dilute the resulting solution to 1.0 liter with distilled water.

2) Magnesium 1000 ppm
   Dissolve 1.0 g of magnesium ribbon in 50 mL of 1:1 hydrochloric acid and dilute to 1.0 liter with distilled water.

3) Strontium 10%
   Dissolve 76.06 g of strontium chloride ($SrCl_2 \cdot 6H_2O$) in distilled water and dilute to 250 mL with distilled water.

Standards

1) Prepare a set of standard solutions containing 0.5, 1.0, 2, 4, and 6 ppm Ca and Mg containing enough Sr solution to obtain a 1% Sr solution in the final dilution.

Samples

1) Prepare the sample by diluting an aliquot of sample containing 1% Sr solution in the final dilution so that the expected reading will fall within the range of the standard curve.

Parameters

1) Calcium
   Wavelength nm 422.7
   Lamp current mA 7
   Bandpass nm 1.0
   Flame description - air-acetylene
   - oxidizing, fuel lean, blue

2) Magnesium
   Wavelength nm 285.2
   Lamp current mA 3
   Bandpass nm 1.0
   Flame description - air-acetylene
   - oxidizing, fuel lean, blue

References

Bentley, E. M. and G. F. Lee. 1967. Determination of calcium in natural water by atomic absorption spectrophotometry. Environ. Sci. Technol. 1: 721.

Butler, L. R. P. and D. Brink. 1963. The determination of magnesium, calcium, potassium, sodium, copper, and iron in water samples by atomic absorption spectroscopy. South African Industrial Chemist 17: 153.

Robinson, J. W. 1966. Atomic absorption spectroscopy. Marcel Dekker, Inc., New York.

ANALYSIS OF MINOR CATIONS

1. COPPER, ZINC, NICKEL, IRON, AND MANGANESE BY ATOMIC ABSORPTION SPECTROPHOTOMETRY

Reagents

1) Ammonium acetate buffer
   1:1, acetic acid: ammonium hydroxide to give a solution of pH 5.5

2) 8.0 M nitric acid
   Dilute 506 mL of HNO_3 (conc.) to 1.0 liter with distilled water.

3) Chelex 100 (50-100 mesh)
   Available from Bio-Rad Laboratories, Mississauga, Ontario.

Standards

Standard	Cu ppm	Zn ppm	Ni ppm	Fe ppm	Mn ppm
1	0.1	0.1	0.3	0.5	0.5
2	0.3	0.3	1.0	1.0	1.0
3	1.0	1.0	3.0	3.0	3.0
4	2.0	2.0	5.0	5.0	5.0
5	5.0	5.0	10.0	10.0	10.0

NOTE: All standards diluted to volume with 8.0 M HNO_3.

Sample Preparation

1) Add 2 mL of buffer solution for each 100 mL of sample used (pH should be 5.5 $\pm$ 0.2).

2) Pass the sample through a 1 x 10 cm Chelex 100 column at a rate of $\leq$ 10 mL/min.

3) Pass 20 mL of buffer solution through the column at a rate of approximately 2 mL/min.

4) Collect the elutant by passing 25 mL of 8.0 M HNO_3 through the column at a rate of 1.5 mL/min.

NOTE: When determination of Fe is to be done, use a volume of 500 mL maximum. For Cu, Zn, Ni, and Mn, use a volume of 500 mL to 1.0 liter. The order of selectivity for Chelex 100 ion exchange resin is as follows: H > L; > Na > K > Cu > Pb > Fe > Al > Cr > Ni > Zn > Ag > Co > Cd > Mn > Ba > Ca.

Instrument Parameters

Most atomic absorption spectrophotometers are supplied with a "cookbook" of parameters that the manufacturer has tested for his instrument. The following list of parameters applies to an International Laboratory Model S11 aa/ae spectrophotometer.

Element	Wavelength nm	Lamp current	Bandpass	Flame description
Cu	324.7	5	1.0	Oxidizing, fuel lean, blue
Fe	248.3	8	0.3	Oxidizing, fuel lean, blue
Ni	232.0	10	0.15	Oxidizing, fuel lean, blue
Zn	213.9	3	1.0	Oxidizing, fuel lean, blue
Mn	279.5	5	0.5	Oxidizing, fuel lean, blue

NOTE: All flame descriptions are for flames containing air and acetylene.

References

Biechler, D. G. 1965. Determination of trace copper, lead, zinc, cadmium, nickel, and iron in industrial waste waters by atomic absorption spectrometry after ion exchange concentration on Dowex A-1. Analytical Chemistry 37(8): 1054-1055.

Robinson, J. W. 1966. Atomic absorption spectroscopy. Marcel Dekker, Inc., New York.

Standard methods for the examination of water and waste water including bottom sediments and sludges. 1976. Fourteenth edition. American Public Health Association, Inc., New York.

2. IRON (Fe) BY SPECTROPHOTOMETRY

Iron must be supplied for proper plant growth and development. It functions in the production of chlorophyll although it does not enter into the chemical composition of chlorophyll. It appears to function as a catalyzer working through the important enzymes such as dehydrogenases, carboxylases, kinases, oxidases, and peroxidases necessary for certain respiratory processes. In limnological literature, there are reports that iron may be involved in the reduction of nitrates to nitrites by ferrous salts in the presence of oxygen and the reduction of dissolved oxygen in the presence of iron.

Reagents

1) HCl concentrate

2) Ethylenediamine - full strength

3) Hydroxylamine
   Dissolve 10 g $NH_2OH \cdot HCl$ in 100 mL distilled water.

4) Tripyridine solution
   Dissolve 0.1 g of 2, 2', 2'' tripyridine in 100 mL 0.1N HCl and gently warm on a hot plate.

5) Stock iron solution
   Slowly add 20 mL concentrated H_2SO_4 to 50 mL distilled water and dissolve 1.404 g ferrous ammonium sulfate, $Fe(NH_4)_2 \cdot 6H_2O$ in this solution. Add 0.1N $KMnO_4$ until a faint color persists. Dilute solution to 1.0 liter with iron-free distilled water.

Standard Iron Solution

1) Pipette 50 mL of stock solution into a 1.0-liter volumetric and dilute to 1.0 liter with iron-free distilled water. 1.0 mL = 10 µg Fe.

2) Pipette 5 mL of stock solution into a 1.0-liter volumetric and dilute to 1.0 liter with iron-free distilled water. 1.0 mL = 1.0 µg Fe.

Calibration Curve (555 mµ)

1) Pipette 1.0, 2, 3, 4, 5, 7, 10, 15, and 20 mL of standard solution A into 50-mL volumetrics and dilute to the mark with iron-free distilled water.

2) Pipette 1.0, 2, 3, 4, 5, 7, and 10 mL of standard solution B into 50-mL volumetrics and dilute to the mark with iron-free distilled water.

3) Pour the solutions into 125-mL Erlenmeyer flasks.

4) Add 2 mL concentrated HCl and boil the solutions to ensure dissolution of all the iron. Cool the solutions to room temperature.

5) Add 1.0 mL hydroxylamine solution, 5 mL ethylenediamine, and 5 mL tripyridine solution to each flask.

6) Dilute the solutions to 50 mL in volumetric flasks.

7) Read the % transmittance at 555 mμ of the solutions against a blank of distilled water.

8) Prepare a calibration curve of absorbance vs concentration of Fe (ppm).

9) To convert iron concentrations from parts per million to milliequivalents per million, multiply ppm by 0.0358 for ferrous ion and 0.0537 for ferric ion.

Sample Procedure

1) Pipette 50 mL of sample into a 125-mL Erlenmeyer flask.

2) Follow steps 4 to 7 inclusive of the procedure for the calibration curve.

3) Read the unknown concentration of the sample off the calibration curve.

Reference

Standard methods for the examination of water and waste water including bottom sediments and sludges. 1976. Fourteenth edition. American Public Health Association, Inc., New York.

3. COPPER (Cu) BY SPECTROPHOTOMETRY

Copper has been shown to be a requirement for photosynthesis in algae through the pigment plastocyanin and probably is implicated in the electron transport mechanism of the plastocyanin. Copper is also an essential component of the enzymes ascorbic acid oxidase, tyrosinane, laccose, monoamine oxidase, cytochrome oxidase, and galatose oxidase.

Reagents

1) Copper-free water
   Redistill distilled water in an all-Pyrex glass system.

2) Stock copper solution
   Dissolve 0.1 g copper foil in 3 mL distilled water and 3 mL concentrated HNO_3 in a fume hood. Cover the beaker with a watch glass. After all the metal has dissolved, add 1.0 mL concentrated H_2SO_4 and heat on a hot plate. Stop heating the solution just before complete dryness. Cool and dissolve the solution in copper-free water and dilute to 1.0 liter. 1.0 mL = 0.1 µg Cu.

3) Standard copper solution
   Dilute 50 mL of stock copper solution to 1.0 liter with copper-free water. 1.0 mL = 5 µg Cu.

4) HCl
   Dilute 1:1 with distilled water.

5) Sodium pyrophosphate solution
   Dissolve 30 g $Na_4P_2O_7 \cdot 10H_2O$ in copper-free water and dilute to 1.0 liter.

6) Sodium acetate solution
   Dissolve 400 g $NaC_2H_3O_2 \cdot 3H_2O$ in 600 mL of copper-free water.

7) Cuprethol reagent mixture
   Solution I - Dissolve 4 g diethanolamine in 200 mL methyl alcohol. Solution II - Dissolve 3 mL carbon disulfide in 200 mL methyl alcohol. Prepare the reagent by mixing equal volumes of the two solutions just before the determination is to be made.

Calibration Curve

1) Pipette 0.0, 0.5, 1.0, 2, 3, 4, 6, 8, and 10 mL standard copper solution into 100-mL volumetrics and dilute to the mark.

2) Add 0.5 mL HCl and mix. Add 2 mL sodium pyrophosphate solution and mix.

3) Pour the solutions into 125-mL Erlenmeyer flasks.

4) Add 2 mL concentrated HCl and boil the solutions to ensure dissolution of all the iron. Cool the solutions to room temperature.

5) Add 1.0 mL hydroxylamine solution, 5 mL ethylenediamine, and 5 mL tripyridine solution to each flask.

6) Dilute the solutions to 50 mL in volumetric flasks.

7) Read the % transmittance at 555 mμ of the solutions against a blank of distilled water.

8) Prepare a calibration curve of absorbance vs concentration of Fe (ppm).

9) To convert iron concentrations from parts per million to milliequivalents per million, multiply ppm by 0.0358 for ferrous ion and 0.0537 for ferric ion.

Sample Procedure

1) Pipette 50 mL of sample into a 125-mL Erlenmeyer flask.

2) Follow steps 4 to 7 inclusive of the procedure for the calibration curve.

3) Read the unknown concentration of the sample off the calibration curve.

Reference

Standard methods for the examination of water and waste water including bottom sediments and sludges. 1976. Fourteenth edition. American Public Health Association, Inc., New York.

3. COPPER (Cu) BY SPECTROPHOTOMETRY

Copper has been shown to be a requirement for photosynthesis in algae through the pigment plastocyanin and probably is implicated in the electron transport mechanism of the plastocyanin. Copper is also an essential component of the enzymes ascorbic acid oxidase, tyrosinane, laccose, monoamine oxidase, cytochrome oxidase, and galatose oxidase.

Reagents

1) Copper-free water
   Redistill distilled water in an all-Pyrex glass system.

2) Stock copper solution
   Dissolve 0.1 g copper foil in 3 mL distilled water and 3 mL concentrated HNO_3 in a fume hood. Cover the beaker with a watch glass. After all the metal has dissolved, add 1.0 mL concentrated H_2SO_4 and heat on a hot plate. Stop heating the solution just before complete dryness. Cool and dissolve the solution in copper-free water and dilute to 1.0 liter. 1.0 mL = 0.1 µg Cu.

3) Standard copper solution
   Dilute 50 mL of stock copper solution to 1.0 liter with copper-free water. 1.0 mL = 5 µg Cu.

4) HCl
   Dilute 1:1 with distilled water.

5) Sodium pyrophosphate solution
   Dissolve 30 g $Na_4P_2O_7 \cdot 10H_2O$ in copper-free water and dilute to 1.0 liter.

6) Sodium acetate solution
   Dissolve 400 g $NaC_2H_3O_2 \cdot 3H_2O$ in 600 mL of copper-free water.

7) Cuprethol reagent mixture
   Solution I - Dissolve 4 g diethanolamine in 200 mL methyl alcohol. Solution II - Dissolve 3 mL carbon disulfide in 200 mL methyl alcohol. Prepare the reagent by mixing equal volumes of the two solutions just before the determination is to be made.

Calibration Curve

1) Pipette 0.0, 0.5, 1.0, 2, 3, 4, 6, 8, and 10 mL standard copper solution into 100-mL volumetrics and dilute to the mark.

2) Add 0.5 mL HCl and mix. Add 2 mL sodium pyrophosphate solution and mix.

3) Adjust the pH to 5-6 with sodium acetate and let stand for 5 minutes.

4) Add 1.0 mL cuprethol reagent mixture.

5) Allow the solution to stand for 10 minutes but not longer than 30 minutes.

6) Read the % transmittance at 435 mμ of the solution.

7) Plot a calibration curve of absorbance vs concentration of copper (ppm).

8) To convert copper concentrations from parts per million to milliequivalents per million, multiply by 0.0315.

Sample Procedure

1) Pipette a 100-mL sample into a 250-mL beaker.

2) Follow steps 2 to 6 inclusive of the calibration curve procedure.

3) From the calibration curve, determine the concentration of copper in the sample.

Reference

Standard methods for the examination of water and waste water including bottom sediments and sludges. 1976. Fourteenth edition. American Public Health Association, Inc., New York.

4. BORON (B) BY SPECTROPHOTOMETRY

Reagents

1) Stock boron solution
   Dissolve 0.5716 g anhydrous boric acid, H_3BO_3, in distilled water and dilute to 1.0 liter. 1.0 mL = 0.1 µg B.

2) Standard boron solution
   Dilute 100 mL stock boron solution to 1.0 liter with distilled water. 1.0 mL = 10 µg B.

3) HCl
   Concentrated.

4) HCl
   Dilute 1:11 with water.

5) Sulfuric acid
   Concentrated.

6) Carmine reagent
   Dissolve 0.92 g carmine N.F. 40 in 1.0 liter concentrated H_2SO_4.

Calibration Curve

1) Pipette 1.0, 2.5, 5, 7.5, and 10 mL standard boron solution into 100-mL volumetric flasks and dilute with distilled water.

2) Pipette 2 mL of each solution into a 30-mL test tube.

3) Add 2 drops concentrated HCl; then carefully add 10 mL concentrated H_2SO_4. Mix the solution and cool to room temperature.

4) Add 10 mL carmine reagent and mix thoroughly.

5) After 45 to 60 minutes, take the % transmittance at 585 mµ.

6) Plot a calibration curve of absorbance vs concentration of Boron (ppm).

Sample Procedure

1) Evaporate 100 mL of sample to dryness in an evaporating dish that can withstand temperatures greater than 550°C.

2) Ignite the residue remaining in the evaporating dish at 550°C for 1 hour to destroy any organic material.

3) Acidify the cooled residue with 3 mL 1:11 HCl.

4) Pipette 2-mL sample into a 30-mL test tube.

5) Follow steps 3 to 5 inclusive of the procedure for the calibration curve.

6) Read the sample concentration off the calibration curve.

Reference

Standard methods for the examination of water and waste water including bottom sediments and sludges. 1976. Fourteenth edition. American Public Health Association, Inc., New York.

5. MOLYBDENUM (Mo) BY SPECTROPHOTOMETRY

Molybdenum is involved in the nitrogen metabolism of higher plants and algae through the nitrate reductase system.

Reagents

1) Concentrated HCl - sp gr 1.16

2) Potassium thiocyanate
   Dissolve 10 g potassium thiocyanate in water and dilute to 100 mL.

3) Stannous chloride
   Dissolve 10 g stannous chloride in 1:9 HCl. Prepare this solution as needed.

4) Ethyl ether
   Shake pure ether with 1/10 its volume of a mixture of potassium thiocyanate and stannous chloride solutions immediately before use.

5) Stock molybdenum solution
   Dissolve 0.552 g ammonium molybdate, $(NH_4)_6Mo_7O_{24}\cdot H_2O$, in water and dilute to 1.0 liter.

6) Standard molybdenum solution
   Dilute 10 mL stock molybdenum solution to 100 mL. 1.0 mL = 30 µg Mo.

Calibration Curve

1) Pipette 1.0, 2, 3, 4, and 5 mL of standard molybdenum solution into separatory funnels.

2) Dilute each solution to 50 mL with water.

3) Add 7 mL concentrated HCl and mix thoroughly.

4) Add 3 mL potassium thoicyanate and 3 mL stannous chloride solution.

5) Extract the solution with 10 mL ether followed by four 5-mL portions. Collect the ether extracts in a 10-mL cuvette.

6) Read the % transmittance at 470 mµ of each solution.

7) Draw a calibration curve of absorbance vs concentration of molybdenum.

8) To convert molybdenum concentrations from parts per million to milliequivalents per million, multiply by 0.0624.

NOTE: To prevent ether from evaporating into the atmosphere, keep the solutions covered.

Sample Procedure

1) Pipette a 100-mL sample into a 250-mL beaker. Evaporate this to near dryness.

2) Add 10 mL concentrated HCl.

3) Transfer the solution to a 100-mL beaker and dilute to 40 mL with distilled water.

4) Boil the solution for a few minutes and transfer it to a 100-mL volumetric. If the solution is turbid, filter it through a No. 44 Whatman filter paper and wash it with hot water.

5) Transfer a 50-mL aliquot to a separatory funnel and add 2 mL concentrated HCl.

6) Add 3 mL potassium thiocyanate and 3 mL stannous chloride.

7) After 1 minute, add 10 mL ether and shake the mixture vigorously for about 30 seconds. Vent the solution carefully so as not to lose any of the solution.

8) When the two layers have separated, run the ether layer into a 10-mL cuvette.

9) Reextract the aqueous layer with 5 mL ether. (Two extractions should be sufficient to remove most of the color. However, if the ether layer is not colorless, an additional extraction may be necessary.)

10) Read the % transmittance at 470 mμ of the sample and determine the concentration from the calibration curve.

Reference

Piper, C. S. 1951. Soil and plant analysis. Interscience Publishers, Inc., New York.

6. COBALT (Co) BY SPECTROPHOTOMETRY

Cobalt is an essential constituent of the vitamin B_{12} coenzymes, which are intimately involved in formate and methyl group metabolism. Propionate metabolism is also regulated by vitamin B_{12}.

Reagents

1) Standard cobalt solution
   Dissolve 0.4037 g pure cobalt chloride, $CoCl_2 \cdot 6H_2O$, in distilled water and add 10 mL hydrochloric acid and dilute to 1.0 liter. 1.0 mL = 100 µg Co.

2) HCl
   Dilute 1:2 with water.

3) HCl 0.5N
   Dilute 45 mL concentrated HCl to 1.0 liter.

4) HNO_3
   Dilute 1:1 with water.

5) KOH
   Dissolve 10 g KOH in water and dilute to 100 mL.

6) Phenolphthalein solution
   Dissolve 0.2 g phenolphthalein in 100 mL ethanol.

7) Nitroso-R-salt
   Dissolve 0.1 g pure crystals in water and dilute to 100 mL.

Calibration Curve

1) Dilute suitable aliquots of standard cobalt solution to 15 mL.

2) Add 8 drops dilute HNO_3 and 1.0 mL dilute HCl to each solution.

3) Add 2 mL nitroso-R-salt followed by 2 g sodium acetate.

4) Heat to †70°C and add 6 drops phenolphthalein solution.

5) Add KOH solution until a pink color just appears.

6) Add 0.5N HCl until the pink color is just discharged.

7) Heat the solution to just below the boiling point for exactly 2 minutes, adding, if necessary, 0.5N HCl if the solution turns alkaline.

8) Add 5 mL dilute HNO_3 and boil for another 2 minutes.

9) Cool immediately under a cold water tap.

10) Dilute to a volume of 25 mL in the dark.

11) Read the % transmittance at 400 mμ.

12) Plot a calibration curve of absorbance vs concentration of cobalt (ppm).

13) To convert cobalt concentrations from parts per million to milli-equivalents per million, multiply ppm by 0.0339.

Sample Procedure

1) Pipette a 100-mL sample into a 250-mL beaker.

2) Evaporate the sample to dryness.

3) Add enough water to make the solution up to 10 mL.

4) Add 1.0 mL dilute HCl and 8 drops dilute HNO_3.

5) Heat the solution to just below the boiling point for a few minutes, cool, and add 2 mL nitroso-R-salt and 2 g sodium acetate.

6) Follow steps 4 to 13 inclusive of the procedure for the calibration curve.

7) From the calibration curve, read the concentration of cobalt in the sample.

Reference

Piper, C. S. 1951. Soil and plant analysis. Interscience Publishers, Inc., New York.

7. ZINC (Zn) BY SPECTROPHOTOMETRY

Zinc is an essential constituent of alcohol dehydrogenase, glutamic dehydrogenase, lactic dehydrogenase, carbonic anhydrase, alkaline phosphatase, and carboxypeptidose B_1. In algae, the oxidation of acetate and ethanol is depressed by zinc deficiency. Zinc deficiency appears to inhibit the synthesis of protein from RNA.

Reagents

1) Zinc-free water
   Redistill distilled water in an all-Pyrex glass system.

2) Stock zinc solution
   Dissolve 0.1 g 30-mesh zinc metal in a slight excess of 1 + 1 HCl (≈ 1 mL). Dilute the solution to 1.0 liter with zinc-free water. 1.0 mL = 0.1 mg Zn.

3) Standard zinc solution
   Dilute 10 mL zinc stock solution to 1.0 liter with zinc-free water. 1.0 mL = 1.0 µg Zn.

4) HCl 0.02N
   Dilute 1.0 mL concentrated HCl to 600 mL with zinc-free water.

5) Sodium acetate 2N
   Dissolve 68 g $NaC_2H_3O_2 \cdot 3H_2O$ and dilute to 250 mL with zinc-free water.

6) Acetic acid
   Dilute 1 to 7 with distilled water.

7) Acetate buffer solution
   Mix equal volumes of 2N sodium acetate solution and dilute acetic acid solution. Extract with 10-mL portion of dithizone solution I until the last extract remains green, then extract with carbon tetrachloride to remove excess dithizone.

8) Sodium thiosulfate solution
   Dissolve 25 g $Na_2S_2O_3 \cdot 5H_2O$ in 100 mL of zinc-free water. Purify by dithizone extraction as for acetate buffer solution.

9) Dithizone solution I
   Dissolve 0.1 g diphenyl thicarbozone in 1.0 liter of carbon tetrachloride. Store this solution in an amber glass bottle in the refrigerator.

10) Dithizone solution II
    Dilute 1 volume of dithizone solution I with 9 volumes of CCl_4. Store in an amber glass bottle in the refrigerator.

11) Carbon tetrachloride

12) Sodium citrate solution
Dissolve 10 g $Na_3C_6H_5O_7 \cdot 2H_2O$ in 90 mL zinc-free water. Purify by dithizone extraction as for acetate buffer solution. This solution is used for final cleansing of glassware.

13) To convert zinc concentrations from parts per million to milliequivalents per million, multiply ppm by 0.0306.

NOTE: Wash all glassware with dilute HNO_3, then wash with zinc-free water. Then rinse all glassware with sodium citrate solution.

Calibration Curve

1) To a series of 125-mL Squibb separatory funnels, thoroughly cleansed, add 0.0, 1.0, 2, 3, 4, and 5 mL of standard zinc solution.

2) Bring each volume up to 10 mL by adding zinc-free water.

3) To each funnel, add 5 mL acetate buffer and 1.0 mL sodium thiosulfate solution and mix thoroughly (pH should be between 4 and 5.5).

4) To each funnel, add 10 mL dithizone solution II. Stopper and shake vigorously for 4 min.

5) Allow the layers to separate. Dry the stem of the funnel with strips of filter paper and run the lower CCl_4 layer into a dry, clean cuvette.

6) Read the % transmittance at 535 mμ of each solution against the blank.

7) Plot a graph of absorbance vs concentration of zinc (ppm).

Sample Procedure

1) Pipette 10 mL of sample into a 125-mL separatory funnel.

2) Follow steps 3 to 6 inclusive of the procedure for the calibration curve.

3) Read the concentration of the sample off the calibration curve.

Reference

Standard methods for the examination of water and waste water including bottom sediments and sludges. 1976. Fourteenth edition. American Public Health Association, Inc., New York.

ANALYSIS OF MAJOR ANIONS

1. CHLORIDES (Cl^-) BY TITRATION TO SILVER CHLORIDE ENDPOINT

Reagents

1) Standard silver nitrate solution
   Weigh 1.7 g $AgNO_3$ into a beaker. Dry at 110°C for 1 hour. Cool. Reweigh the beaker and $AgNO_3$ to find the actual dry weight. Empty the $AgNO_3$ into a 1.0-liter volumetric flask. Reweigh the beaker to find the actual amount of $AgNO_3$ in the solution. The standard solution should be approximately 0.01N. Calculate the actual normality of the solution.

2) Sodium bicarbonate

3) Potassium chromate (K_2CrO_4) - 5.0%
   Weigh out 25 g of K_2CrO_4 and dilute it to 500 mL with distilled water in a volumetric flask.

Sample Procedure

1) Pipette 100 mL of sample into a 250-mL Erlenmeyer flask.

2) Add a pinch of sodium bicarbonate and wait until effervescence stops.

3) Add 1.0 to 2 mL of 5.0% K_2CrO_4 solution.

4) Titrate the sample with 0.01N $AgNO_3$ until the first permanent appearance of the buff (red-brown) silver chromate color.

5) Do a blank run with distilled water.

Calculations

1) Normality of standard $AgNO_3$ solution

$$NAgNO_3 = \frac{(\text{wt of } AgNO_3 \text{ (mg) x purity factor})/\text{eq wt } AgNO_3}{1000 \text{ mL}}$$

eq wt $AgNO_3$ = 169.90

2) Sample calculation

$$\text{ppm Cl} = \frac{(V-B) \times 35.457 \times 1000 \times N}{\text{mL of sample}}$$

V = mL of $AgNO_3$ used for sample

B = mL of $AgNO_3$ used for blank determination

N = Normality of standard $AgNO_3$

3) To convert chloride concentrations from parts per million to milli-equivalents per million multiply ppm by 0.0282.

Reference

Skoog, D. A. and D. M. West. 1966. Fundamentals of analytical chemistry. Holt, Rinehart, and Winston, New York.

2. CHLORIDES (Cl^-) BY TITRATION TO PHENOLPHTHALEIN ENDPOINT

Reagents

1) Chloride-free water
   Purify distilled water by redistilling distilled water in an all-pyrex glass apparatus.

2) Potassium chromate indicator solution
   Dissolve 50 g of K_2CrO_4 in a small amount of distilled water. Add silver nitrate solution until a definite red precipitate is formed. Allow to stand for at least 12 hours, then filter and dilute the filtrate to 1.0 liter with distilled water.

3) Standard silver nitrate titrant (0.0141N)
   Dissolve 2.396 g of $AgNO_3$ in distilled water and dilute to 1.0 liter. Store in an amber bottle. Standard $AgNO_3$ of 0.0141N = 0.5 mg Cl/1.0 mL.

4) Standard NaCl (0.0141N)
   Dissolve 0.8241 g NaCl (dried at 140°C for a few hours) in chloride-free water and dilute to 1.0 liter. 1.0 mL = 0.5 mg Cl.

5) Aluminum hydroxide suspension
   Refer to procedure of nitrates under the heading of reagents.

6) Phenolphthalein indicator solution
   Dissolve 5 g of phenolphthalein in 500 mL of 95% ethanol and add 500 mL of distilled water. Add 0.02N NaOH dropwise until a faint pink color appears.

7) Sodium hydroxide (1N)
   Dissolve 40 g NaOH in distilled water and dilute to 1.0 liter.

8) Sulfuric acid (1N)
   Add 28 mL of concentrated H_2SO_4 to distilled water, cool, and dilute to 1.0 liter.

9) Hydrogen peroxide 30%.

Sample Procedure

A) Standardization of $AgNO_3$ solution

   1) Adjust the pH of 10 mL of NaCl solution to pH 7-10 with 1N H_2SO_4 or 1N NaOH.

   2) Add 1.0 mL H_2CrO_4 indicator solution.

   3) Titrate with standard $AgNO_3$ to a pinkish-yellow endpoint.

B) Calculation

$V_1N_1 = V_2N_2$

V_1 = Volume of $AgNO_3$

N_1 = Normality of standard $AgNO_3$ (unknown)

V_2 = Volume of NaCl solution

N_2 = Normality of NaCl solution

$$N_1 = \frac{V_2N_2}{V_1}$$

C) Sample treatment

1) Pipette 100-mL sample or a suitable aliquot diluted to 100 mL into a flask.

2) If the sample is colored, add 3 mL $Al(OH)_3$ suspension, mix, allow the solution to settle, filter the solution, wash, and combine filtrate and washing(s).

3) If sulfide, sulfite, or thiosulfate are present, make the solution alkaline to phenolphthalein with NaOH solution. Add 1 mL of H_2O_2 and stir. Neutralize the solution with sulfuric acid.

4) Adjust the pH of the sample from 7-10 with 1N H_2SO_4 or 1N NaOH.

5) Add 1.0 mL K_2CrO_4 indicator solution.

6) Titrate with standard silver nitrate to a pinkish yellow or green endpoint.

7) A blank run should also be done with distilled water.

D) Sample calculation

$$\text{mg/L Cl} = \frac{(V-B) \times N \times 35{,}450}{\text{mL of sample}}$$

V = mL of titrant used

B = mL of titrant used for the blank

N = Normality of standard $AgNO_3$

mg/L NaCl = mg/L Cl x 1.65

E) To convert parts per million to milliequivalents per million, multiply ppm Cl by 0.0282.

References

Skoog, D. A. and D. M. West. 1966. Fundamentals of analytical chemistry. Holt, Rinehart, and Winston, New York.

Standard methods for the examination of water and waste water including bottom sediments and sludges. 1976. Fourteenth edition. American Public Health Association, Inc., New York.

3. FLUORIDES (F^-) BY SPECIFIC ION ELECTRODES

Reagents

1) 100 ppm F
   Dissolve 0.221 g of NaF in distilled water and dilute to 1.0 liter with distilled water.

2) Total ionic strength adjustment buffer (TISAB) for complexing samples with less than 5 ppm Al and/or Fe
   Place approximately 500 mL of distilled water into a 1.0-liter beaker. Add 57 mL glacial acetic acid, 58 g NaCl, and 4 g CDTA (1,2 diamino-cyclohexane N,N,N'N'-tetracetic acid or cyclohexylene dinitrilo tetraacetic acid) and dissolve. Cool the solution. Adjust the pH to 5.0-5.5 with NaOH. Cool and dilute to 1.0 liter with distilled water.

   TISAB for complexing sample with greater than 5 ppm Al and/or Fe
   Place approximately 500 mL of distilled water in a 1.0-liter beaker. Add 84 mL concentrated HCl, 242 g TRIS (hydroxymethyl) amino methane, and 230 g sodium tartrate and dissolve. Cool and dilute to 1.0 liter with distilled water.

Meter Calibration - Direct Measurement (ppm)

For Model 404 Ionanalyzer with a fluoride electrode.

1) Prepare a set of standard solutions of the following concentrations, 1.0 and 0.1 ppm F by serial dilution.

2) Pipette 25 mL of each standard into a beaker. Add 25 mL of the appropriate buffer solution.

3) Place the electrode(s) in the 1.0 ppm F^- solution and turn the function switch to F^-. Adjust the meter to read 100 on the red scale with the calibration knob.

4) Rinse and dry the electrode(s).

5) Place the electrode(s) in the 0.1 ppm F solution and turn the function switch to F^-. Adjust the meter to read 10 on the red scale with the temperature compensator knob.

6) All readings in direct units will be divided by 100.

Sample Readings

1) Pipette 25 mL of sample into a beaker.

2) Add 25 mL of the appropriate buffer.

3) Turn the function switch to F^-.

4) Divide the reading taken by 100.

NOTE: A conventional pH meter can be used on the millivolt scale. A calibration curve can be drawn from the millivolt readings take. The concentration of fluoride can be determined from the calibration curve. All samples should be constantly stirred during reading.

References

Analytical Methods Guide. 1975. Orion Research. 7th edition.

Fluoride electrodes. 1977. Orion Research Inc. Form IM94,96-09/7721.

4. SULFATES (SO_4) BY COLUMN CHROMATOGRAPHY AND TITRATION

Sulfur appears necessary for cell division in algae nutrition suggesting a possible role for S-containing nucleotides derived from sulfate after reduction. Sulfur is also necessary for the synthesis of the amino acids methionine, glutathione, cysteine, and homocysteine. Polysaccharides with ester sulfates have also been found in brown algae Chlorella and Scenedesmus. In higher plants, cysteine, methionine, homocysteine, lipoic acid, coenzyme A, glutathione, biotin, adenosine-5'-phosphosulfate, and thiamine pyrophosphate all require sulfur.

Reagents

1) H^+ form resin (50-100 mesh).

2) 2N HCl
   Add 73 mL concentrated HCl to water and dilute to 1.0 liter.

3) Methyl orange indicator solution 0.1%
   Dissolve 0.1 g indicator in distilled water and dilute to 100 mL with distilled H_2O.

4) Methyl red indicator solution 0.1%
   Dissolve 0.1 g indicator in distilled water and dilute to 100 mL with distilled water.

5) 0.1N NaOH
   Boil 1.5 liters of distilled water and cool to room temperature. Prepare a Gooch crucible and wash thoroughly. Weigh 10.0 g NaOH pellets into a 125-mL flask. Add 10 mL distilled water and swirl in the flask. Allow the flask and contents to cool. Filter through a prepared Gooch crucible and collect the clear filtrate in a clean test tube placed inside the filtering flask. Pour 5.0 mL of this solution into the previously cooled water and mix thoroughly. Transfer the solution to a storage bottle.

6) Standardization of 0.1N NaOH
   Dry potassium acid phthlate, $KHC_8H_{14}O_4$, at 110° for 2 hours and cool. Weigh 0.7-0.9 g samples into 250-mL flasks and dissolve in 25 to 30 mL distilled water. Add 2 drops phenolphthalein and titrate with NaOH to the first pink color that persists for 30 seconds.

7) 0.02N NaOH
   Dilute 200 mL standardized 0.1N NaOH to 1.0 liter with distilled water or dilute the required amount of 0.1N NaOH to 1.0 liter to make an exact solution of 0.02N NaOH.

Sample Procedure

1) Prepare an ion exchange column using a 15-25 cm bed of 50-100 mesh resin in a Jones reductor column with a plug of glass wool.

2) Back-wash with distilled water to remove trapped air.

3) Regenerate the column by passing 50 mL 2N HCl through the column at the rate of 20 mL/min.

4) Rinse the column by passing distilled water through the column until the effluent is on the basic side of methyl orange (pH range 3.1-4.4, acid - red, base - yellow).

5) Pipette a 50-mL sample onto the resin bed and allow it to flow through the column at 20 mL/min into a 250-mL Erlenmeyer flask.

6) Wash the resin bed with three 25-mL portions distilled water and collect in 250-mL flask and allow each to drain to just above the resin before adding the next wash.

7) Boil the effluent to remove CO_2, cool, titrate with standard 0.02N NaOH using methyl red (0.1%) indicator.

Calculations

1) Standardization of 0.1N NaOH

$$\text{eq wt KHP} = \frac{\text{mol wt}}{1} = 200.228$$

therefore

$$\text{meq NaOH} = \text{meq } KHC_8H_4O_4$$

$$= \frac{\text{mg } KHC_8H_4O_4 \times \text{purity factor}}{\text{eq wt KHP}}$$

N = meq/mL of titrant used

2) Sample calculations

$$\text{eq wt } SO_4^{=} = \frac{\text{mol wt}}{2} = \frac{96.066}{2} = 48.033$$

2 meq NaOH = 1 meq $SO_4^{=}$

therefore

$$\text{meq NaOH} = \frac{\text{meq } SO_4^{=}}{2}$$

$$\text{mg } SO_4^{=} = \text{meq } SO_4 \text{ x eq wt } SO_4^{=}$$

$$= \frac{\text{V NAOH x N NaOH}}{2} \text{ x } 48.033$$

$$\text{ppm } SO_4^{=} = \text{V NaOH x N NaOH x } 480.33$$

V NaOH = Volume of NaOH required for the titration

N NaOH = Normality of standardized NaOH

3) To convert sulfate concentrations from parts per million to milli-equivalents per million multiply ppm by 0.0208.

References

Skoog, D. A. and D. M. West. 1966. Fundamentals of analytical chemistry. Holt, Rinehart, and Winston. New York.

Standard methods for the examination of water and waste water including bottom sediments and sludges. 1976. Fourteenth edition. American Public Health Association, Inc., New York.

5. SULFITES (SO_3) BY TITRATION

Reagents

1) Sulfuric acid
   To 250 mL distilled water, add 250 mL concentrated sulfuric acid. Cool and dilute to proper volume.

2) Starch indicator
   Soluble starch powder.

3) Standard potassium iodide-iodate titrant (0.0125N)
   Dissolve 0.4458 g anhydrous potassium iodate, KIO_3 (previously dried for 2 hours at 120°C); 4.35 g potassium iodide, KI; and 0.31 g sodium bicarbonate, $NaHCO_3$; in distilled water and dilute the solution to 1.0 liters. 1 mL = 0.5 mg $SO_3^=$.

4) Dilute 100 mL of 0.0125N KI-KIO_3 to 1.0 liter
   1 mL = 0.50 mg $SO_3^=$. Solution = 0.00125N.

Sample Procedure

1) Collect a fresh water sample with as little air as possible. Cool hot sample to less than 50°C.

2) Add 1.0 mL sulfuric acid to a 250-mL Erlenmeyer flask.

3) Add 50 mL water sample to the flask.

4) Add 0.1 g soluble starch powder.

5) Titrate the sample with standard potassium iodide-iodate titrant until a faint blue color persists.

Calculations

1) $$\text{ppm} = \text{mg/liter } SO_3^= = \frac{V \times N \times 40{,}000}{\text{mL of sample}}$$

   V = Volume of titrant required

   N = Normality of KI - KIO_3 standard solution

2) To convert sulfite concentrations from parts per million to milli-equivalents per million multiply ppm by 0.0250.

Reference

Standard methods for the examination of water and waste water including bottom sediments and0sludges. 1976. Fourteenth edition. American Public Health Association, Inc., New York.

ANALYSIS OF MISCELLANEOUS WATER QUALITY PARAMETERS

1. SPECIFIC CONDUCTANCE OF WATER

Reagents

1) 0.1 N potassium chloride
   Dissolve 1.864 g of previously dried KCl in distilled water and dilute to 250 mL.

2) Prepare a series of solutions containing 0.01 N, 0.001 N, and 0.0001 N KCl.

Calibration and Conductance Cell

1) Pour enough 0.0001 N KCl into a beaker so that the conductance cell can be completely immersed in the solution.

2) Record the reading of the conductance of the solution.

3) Repeat steps 1 and 2 with the other potassium chloride solutions.

4) Correct the observed conductance with an appropriate temperature factor listed in the table below.

5) Calculate the cell factor by averaging the corrected readings.

Sample Procedure

1) Pour enough sample into a beaker as before.

2) Record the reading of the conductance of the sample.

3) Correct the observed conductivity of the sample by multiplying it by the cell factor and temperature factor.

Calculations

1) Cell factor (for platinum black conductance cell)

$$\text{Cell factor (C.F.)} = \frac{C}{A \times B}$$

A = observed conductivity
B = temperature factor corrected to 25°C (from Table I)
C = actual value of conductance of KCl (from Table II)

2) Sample

Corrected specific conductance (μmho/cm) = A x B x C.F.

A = observed conductivity
B = temperature factor corrected to 25°C (from Table I)
C.F. = cell factor (from section A above)

3) To convert μmho/cm to dS/m multiply μmho/cm by 10.

Table I

Temp. °C	Factor	Temp. °C	Factor
0	1.7875	24	1.020
5	1.5750	25	1.000
10	1.3813	26	0.980
15	1.2150	27	0.960
20	1.100	28	0.940
21	1.080	29	0.920
22	1.060	30	0.900
23	1.040		

Table II

N KCl	S.C.*
0.0001	14.94
0.0010	147.0
0.0100	1,413
0.1000	12,880

*Specific conductance in μmho/cm.

References

Maron, S. H. and C. F. Prutton. 1965. Principles of physical chemistry. 4th edition. Macmillian Company, New York.

Moore, W. J. 1972. Physical chemistry. 4th edition. Prentice-Hall Inc., Englewood Clifts, New Jersey.

Standard methods for the examination of water and waste water including bottom sediments and sludges. 1976. Fourteenth edition. American Public Health Association, Inc., New York.

Willard, H. H., L. L. Merritt and J. A. Dean. 1965. Instrumental methods of analysis. 4th edition. D. Van Nostrand Co., Inc., Princetown, New Jersey.

2. ALKALINITY (HCO_3, CO_3, OH) BY TITRATION

Water is described as being alkaline when the hydroxyl-ion concentration exceeds the hydrogen-ion concentration. In western Canada, practically all natural waters are alkaline.

Reagents

1) Phenolphthalein (1.0%)
   Dissolve 1.0 g phenolphthalein in 100 mL ethanol.

2) Methyl orange (1.0%)
   Dissolve 1.0 g methyl orange in 100 mL distilled water.

3) H_2SO_4 (0.2N)
   Add 5.55 mL concentrated H_2SO_4 to distilled water and dilute to 1.0 liter.

4) Sodium carbonate (0.2N)
   Dissolve 10.6 g Na_2CO_3 in distilled water and dilute to 1.0 liter.

Standardization of 0.2N H_2SO_4

1) Pipette 10 mL 0.2N Na_2CO_3 into a small beaker.

2) Add 2 drops methyl orange indicator.

3) Titrate the sample from red to an endpoint of orange-red.

4) Calculate the normality of 0.2N H_2SO_4.

5) From this value, calculate the volume required to make 1.0 liter of 0.02N H_2SO_4.

Sample Procedure

1) Pipette 100 mL of sample into a 250-mL Erlenmeyer flask.

2) Add 2 drops phenolphthalein. If P = 0, go to step 4.

3) If P does not equal 0, titrate the sample with 0.02N H_2SO_4 until the solution is colorless. Record the volume as "P."

4) Add 2 drops methyl orange indicator and titrate the solution to orange-red. Record the total volume used in steps 3 and 4 and "M."

Calculations

A) $NH_2SO_4 = \frac{(\text{mg } Na_2CO_3 \times \text{purity factor})/\text{eq wt } Na_2CO_3}{\text{mL of titration}}$

B) 1) $P > M/2$, OH^- and $CO_3^=$ present

$$\text{ppm } OH^- = \frac{2P-M \times 0.02 \times 17}{0.1}$$

$$\text{ppm } CO_3^= = \frac{2(M-P) \times 0.02 \times 30}{0.1}$$

2) $P = M/2$, $CO_3^=$ present

$$\text{ppm } CO_3^= = \frac{M \times 0.02 \times 30}{0.1}$$

3) $P < M/2$, HCO_3^- and $CO_3^=$ present

$$\text{ppm } HCO_3^- = \frac{(M-2P) \times 0.02 \times 61}{0.1}$$

$$\text{ppm } CO_3^= = \frac{2P \times 0.02 \times 30}{0.1}$$

4) $P = M$, OH^- present

$$\text{ppm } OH^- = \frac{M \times 0.02 \times 17}{0.1}$$

5) $P = 0$, HCO_3^- present

$$\text{ppm } HCO_3^- = \frac{M \times 0.02 \times 61}{0.1}$$

6) a) To convert carbonate concentration from parts per million to milliequivalents per million multiply ppm by 0.0333.

b) To convert biocarbonate concentration to milliequivalents per million multiply ppm by 0.0164.

c) To convert hydroxide concentration to milliequivalents per million multiply ppm by 0.0588.

Reference

Standard methods for the examination of water and waste water including bottom sediments and sludges. 1976. Fourteenth edition. American Public Health Association, Inc., New York.

3. ALKALINITY (HCO_3, CO_3, OH) BY POTENTIOMETRY

Reagents

1) 0.02N H_2SO_4
   Preparation of this reagent is given in the preceding method.

2) Buffer
   Commercially prepared buffers are available for calibration of pH meters.

Sample Procedure

1) Calibrate the pH meter according to the manufacturer's suggested method.

2) Pipette a suitable aliquot of sample into a beaker.

3) Record the pH of the sample.

4) If the pH of the sample is greater than 8.0, titrate the sample to pH 8.0 with 0.02N H_2SO_4. Record this volume as "P."

5) Titrate the sample down to pH 4.0 with 0.02N H_2SO_4. Record this volume as "M."

6) Calculate HCO_3, CO_3, and OH present in the sample as in the previous method.

Reference

Standard methods for the examination of water and waste water including bottom sediments and sludges. 1976. Fourteenth edition. American Public Health Association, Inc., New York.

4. TOTAL WATER HARDNESS BY SPECIFIC ION ELECTRODES

Reagents

1) 1000 ppm $CaCO_3$
   Dissolve 1.467 g of calcium chloride dihydrate in distilled water and dilute to 1.0 liter with distilled water.

2) 1M sodium hydroxide
   Dissolve 40 g NaOH in distilled water. Cool and dilute to 1.0 liter with distilled water.

Meter Calibration - Direct Measurement

For Model 404 Ionanalyzer with a divalent cation electrode plus reference electrode. All solutions should be at pH 7-10; if not, add 1.0 M NaOH to adjust the pH.

1) Prepare a set of standard solutions of the following concentrations, 100 and 10 ppm, by serial dilution.

2) Pipette 25 mL of standard solution into the beaker.

3) Place the electrodes in the 100 ppm $CaCO_3$ solution and turn the function switch to Ca^{++}. Adjust the meter to read 100 on the red scale with the calibration knob.

4) Rinse and dry the electrodes.

5) Place the electrodes in the 10 ppm $CaCO_3$ solution and turn the function switch to Ca^{++}. Adjust the meter to read 10 on the red scale with the temperature compensator knob.

6) All readings will be in ppm $CaCO_3$.

Sample Readings

1) Pipette 25 mL of sample into a beaker.

2) Read the concentration of ppm $CaCO_3$ directly off the red scale.

NOTE: All samples should be constantly stirred during reading.

References

Analytical Methods Guide. 1975. Orion Research. 7th edition.

Divalent cation electrodes. 1977. Orion Research Inc. Form IM93-32/778.

5. TOTAL SOLIDS BY EVAPORATION AND ASHING

Equipment

1) Suitable evaporating dishes that can withstand high temperatures.

2) Drying oven.

3) Hot plates or infrared lamps.

4) Muffle furnace capable of obtaining and maintaining temperatures of 550°C (942°F) or better.

Procedure

1) Take two 100-mL aliquots of sample. Filter one aliquot.

2) Evaporate both samples to dryness on hot plates or under infrared lamps in previously weighed evaporating dishes (tare).

3) Place the aliquots in a drying oven at 100°C for 1 hour.

4) Cook, and weigh each evaporating dish (w_1 - tare).

5) Place the evaporating dishes in a muffle furnace at 525-550°C for 2 hours.

6) Reweigh the dishes after cooling (w_2 - tare).

Calculations

1) Subtract the weight obtained for the filtered sample (F) from that of the unfiltered sample (U).

2) Convert the weight obtained from grams to milligrams.

3) mg x 10 = ppm volatile matter.

4) % volatile matter = $\frac{\text{difference of (U) and (F)}}{\text{wt of (U)}} \times 100\%$

NOTE: The residue resulting from this procedure can be used in the determination of boron in water. Start with Step 3 of the Sample Procedure in the "Analysis of Boron (B) in Water".

6. HUMIC ACIDS BY SPECTROPHOTOMETRY

Humic acids are defined as the decomposition products of plants and animals that comprise the base-soluble, acid- and alcohol-insoluble fractions in the soil.

Reagents

1) Ion exchange resin
   Rexyn 101(H+) or equivalent

2) Hydrochloric acid 0.1 M
   Add 8.3 mL of conc. HCl to distilled water and dilute to 1.0 liter.

3) Sodium hydroxide 0.5 M
   Dissolve 20 g NaOH in distilled water. Cool and dilute to 1.0 liter.

4) Humic acid, natural, for standard solutions - 40 ppm
   Dissolve 20 mg of humic acid in 0.5 M NaOH and dilute to 500 mL.

Calibration Curve

1) Prepare a calibration curve by diluting the standard humic acid solution to make solutions containing 0.1 to 10 ppm.

2) Read the absorbance at 380 mμ.

3) Prepare a calibration curve from the values obtained.

Sample Procedure

1) Pipette a 100-mL aliquot of water into a 250-mL beaker.

2) Evaporate the sample to approximately 20 mL.

3) Pass the water extract through a column of the ion exchange resin.

4) Adjust the pH of the solution to 3 with 0.1 M HCl.

5) Filter the solution.

6) Redissolve the humic acid precipitate in 0.5 M NaOH.

7) Dilute the solution to 25 mL with distilled water.

8) Read the absorbance of the solution at 380 mμ.

9) Determine the humic acid concentration of the sample from the calibration curve.

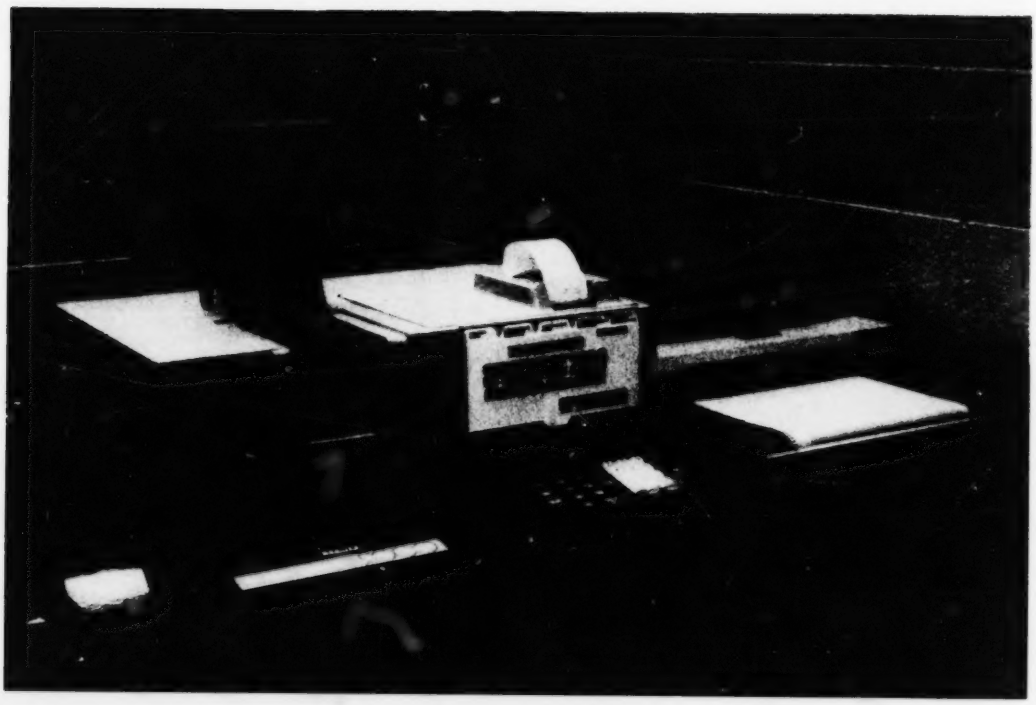
References

Martin, D. F. and Pierce, R. H. 1971. Environmental Letters 1(1): 49-52.

Paakash, A. and Rashid, M. A. 1968. Limnology and Oceanography 13(4): 598-607.

Rashid, M. A. and King, L. H. 1969. Geochimica et Cosmochimica Acta 33(1): 147-151, Pergamon Press.

Water Analysis Laboratory at the Lethbridge Research Station. Left to right, back: refrigeration, washing facilities, glass water distillation apparatus, and stainless steel perchloric acid digestion hood; central bench is work area for processing water samples for individual analyses; right, along wall: automatic column chromatography and ion exchange analysis area; and, foreground: paper and plate chromatography bench.



Bausch and Lomb Spectronic 2000 Spectrophotometer System with integrated microprocessor-controlled automatic background and baseline connection; direct concentration readout with digital display and printer or chart recorder; computer compatibility; multiple repeat scanning and kinetic programming potential; automatic sample collection system; and readings in transmittance, concentration or absorbance.